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***Test Plan to Measure Adsorption of Actinides  
on Interbed Materials from the Radioactive  
Waste Management Complex***



**INEEL**  
IDAHO NATIONAL ENGINEERING & ENVIRONMENTAL LABORATORY

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on Interbed Materials  
from the Radioactive Waste Management Complex**

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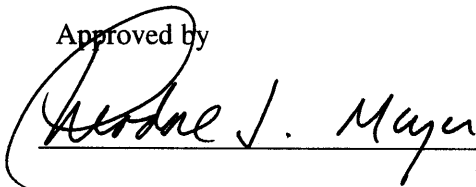
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Approved by

  
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For DKJ

  
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Date

## **ABSTRACT**

The purpose of this investigation is to develop geochemical parameters for a defensible reactive transport model of contaminant migration. This test plan describes objectives, methods, and materials used to measure adsorption of actinides (uranium, neptunium, plutonium, and americium) on interbed materials collected in the vicinity of the Subsurface Disposal Area of the Radioactive Waste Management Complex at the Idaho National Engineering and Environmental Laboratory. The investigation will characterize spatial variation in adsorption parameters in interbeds and determine the effects of variations in vadose zone water chemistry on adsorption. The plan addresses experimental design, measurement protocols, health and safety, and quality control. The study will provide adsorption parameters for contaminants of potential concern to the groundwater pathway at the Subsurface Disposal Area for use in the Operable Unit 7-13/14 remedial investigation/feasibility study.



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## **ACRONYMS**

AA	atomic absorption
ASTM	American Society for Testing and Materials
CEC	cation exchange capacity
COPC	contaminant of potential concern
EPA	U.S. Environmental Protection Agency
EPM	equivalents per million
ICP	inductively coupled plasma emission spectroscopy
INEEL	Idaho National Engineering and Environmental Laboratory
INTEC	Idaho Nuclear Technology and Engineering Center
MCP	management control procedure
OU	operable unit
PSQ	principal study question
RWMC	Radioactive Waste Management Complex
SDA	Subsurface Disposal Area
TDS	total dissolved solids
USGS	U.S. Geological Survey





# **Test Plan to Measure Adsorption of Actinides on Interbed Materials from the Radioactive Waste Management Complex**

## **1. PURPOSE**

The purpose of this investigation is to develop geochemical parameters for a defensible reactive transport model of contaminant migration at the Subsurface Disposal Area (SDA) of the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering and Environmental Laboratory (INEEL). The test plan presents objectives, methods, and materials used to measure adsorption of actinides (uranium, neptunium, plutonium, and americium) on interbed materials collected in the vicinity of the SDA. The primary objectives of the study are to characterize spatial variation in adsorption parameters in interbeds and to determine the effects of variations in vadose zone water chemistry on adsorption. The plan addresses experimental design, measurement protocols, health and safety, and quality control. The study will provide adsorption parameters for contaminants of potential concern (COPCs) to the groundwater pathway at the Subsurface Disposal Area for use in the Operable Unit (OU) 7-13/14 remedial investigation/feasibility study.

The organization of the subsequent sections of this document is as follows:

- Section 2, Project Description. Background information on the need for the project and the data the testing will generate are provided in this section.
- Section 3, Equipment and Materials. The materials that will be included in the testing program and the equipment needed to complete the tests are identified in this section.
- Section 4, Experimental Procedures. The experimental procedures that will be used to acquire the necessary data are identified and discussed in this section.
- Section 5, Waste Management. The management of residual waste is detailed in this section.
- Section 6, Key Project Personnel. Key project personnel are listed in this section.
- Section 7, Quality Assurance/Quality Control. The quality control data that will be collected and the quality assurance program that covers the tests are described in this section.
- Section 8, Deliverables. The results that will be generated by the test plan are discussed in this section.
- Section 9, References. The references used in the test plan are listed in this section.

## 2. PROJECT DESCRIPTION

This section provides background information on why this study is being conducted and what information is needed that the study will generate.

### 2.1 Introduction

Contaminants buried in the SDA of the RWMC at the INEEL may migrate downward over time, carried by infiltration, and reach the Snake River Plain Aquifer. The fate and transport of contaminants is being investigated as part of the OU 7-13/14 remedial investigation/feasibility study. This test plan describes objectives, methods, and materials used to measure adsorption of actinides (uranium, neptunium, plutonium, and americium) on interbed materials collected near the RWMC. The data will be used to assess risk by the groundwater ingestion pathway, evaluate alternative remedial actions, and set quantitative remedial action objectives.

### 2.2 Test Objectives

The transport of an adsorbing contaminant in one dimension is expressed as (Fetter 1993)

$$\left(1 + \frac{\rho}{\theta} K_d\right) \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1)$$

where

$C$	=	concentration (pCi/mL)
$t$	=	time (seconds)
$v$	=	velocity (cm/second)
$\rho$	=	bulk density (g/cm <sup>3</sup> )
$\theta$	=	water content (cm <sup>3</sup> /cm <sup>3</sup> )
$K_d$	=	partition coefficient (mL/g)
$D_L$	=	hydrodynamic dispersion coefficient (cm <sup>2</sup> /second)
$x$	=	distance (cm).

The migration of an adsorbing contaminant is retarded relative to the rate of water movement by the factor  $1 + \rho/\theta K_d$ . The objective of the project is to develop adsorption parameters required for numerical transport modeling of actinides from contaminated waste buried in the SDA to the Snake River Plain Aquifer. Adsorption parameters are used to describe the extent that dissolved chemical species adsorb on solid surfaces, retarding the rate of contaminant migration relative to the movement of water. Adsorption parameters must be representative of the subsurface at the SDA.

## 2.3 Contaminants of Potential Concern

Contaminants of potential concern for OU 7-13/14 were identified in the *Addendum to the Work Plan for the Operable Unit 7-13/14 Waste Area Group 7 Comprehensive Remedial Investigation/Feasibility Study* (DOE-ID 1998). The addendum identified COPCs and the primary exposure pathways (DOE-ID 1998, Table 2-1). Measurement of adsorption parameters is applicable only for transport by the groundwater ingestion exposure pathway. Therefore, only contaminants with groundwater as the primary exposure pathway are considered for this study. A number of the COPCs are known to have very low adsorption characteristics and long half-lives. Better definition of the retardation of Cl-36, I-129, and Tc-99 will have little or no effect on the risk assessment. Carbon-14 adsorption on SDA sedimentary materials has recently been studied (Dicke 1997b), and the results are being published elsewhere. The remaining COPCs are actinides, which have some to significant adsorption onto sediments and moderate to long half-lives. The COPCs for groundwater ingestion include Ac-227, Am-241, Np-237, Pa-231, uranium isotopes of mass 233, 234, 235, 236 and 238. Plutonium isotopes also will be studied.

Actinide elements have been the subject of extensive study for weapons production, reactor fuel production, and radioactive waste management (Choppin and Rydberg 1980; Seaborg and Loveland 1990). The emphasis, however, has been on only a few of the actinide elements, which has left little study for some of the other actinides. An extensive database of thermodynamic data exists for plutonium and uranium for separation of weapons-grade plutonium from uranium fuel elements. A moderate amount of data exists for neptunium and americium. Actinium and protoactinium have not been investigated to any large extent, and essentially no base of thermodynamic data exists for these two elements. There has been, however, a long-standing tradition of using lanthanide elements and other actinide elements as surrogates (Cotton and Hart 1975; Choppin 1995; Gschneidner 1995; Haire 1995). The nature of bonding in the lanthanide and actinide elements is strongly ionic. Therefore, chemical reactions depend on the configuration of electrons—that is, the valence (Choppin 1995). Oxidation state and valence analogs can be used with little or no adjustment (Choppin 1995).

Actinium occurs exclusively in the trivalent oxidation state (Cotton and Hart 1975; Seaborg and Loveland 1990; Haire 1995). Therefore, any of the trivalent lanthanides or actinides will serve as a good surrogate for actinium. The trivalent actinide americium will be used as the analog for actinium. There is no counterpart to protoactinium in the lanthanide series (Haire 1995). Therefore, one of the other actinides must serve as a surrogate for protoactinium. Protoactinium occurs in quadravalent or pentavalent form, with the pentavalent form being somewhat more predominant (Cotton and Hart 1975). In studies of bonding similarities in metallic solids, the elements protoactinium, uranium, and neptunium are most similar (Haire 1995). Based on the bonding similarities to neptunium, and the shared proclivity to the pentavalent oxidation state, neptunium is selected as the analog for protoactinium.

No experimental determinations will be performed for actinium and protoactinium. Adsorption coefficients for americium and neptunium will provide data for predicting adsorption of actinium and protoactinium, respectively.

## 2.4 Principal Study Questions

The purpose of this investigation is to develop geochemical parameters for a defensible reactive transport model of contaminant migration at the SDA. A more complete analysis of the questions and uncertainties involved in the analysis of the adsorption parameters and use in the risk assessment process is needed to ensure that the appropriate data are collected under the appropriate conditions. Data needs and sources of uncertainty were obtained by reviewing the previous risk assessment performed for the

SDA (Magnuson and Sondrup 1998) and a technical review of that risk assessment by the U.S. Geological Survey (USGS) (2000). The principal study questions (PSQs) to be addressed for a defensible reactive transport model of contaminant migration at the SDA are as follows:

- PSQ-1. What are representative, yet conservative,  $K_d$  values for COPCs on interbed material beneath the SDA?
- PSQ-2. Does adsorption follow a linear isotherm or is the adsorption isotherm nonlinear?
- PSQ-3. Is adsorption reversible?
- PSQ-4. What is the effect of water chemistry on adsorption in the vadose zone?
- PSQ-5. Is there a functional relation between material properties of the interbed sediments and adsorption that explains the variability in measured  $K_d$  values?
- PSQ-6. Is there a correlation between hydraulic properties and adsorption that can be used in the development of a spatial distribution of migration characteristics for computer simulation models?

#### **2.4.1 Principal Study Question 1**

Literature review and compilation of the limited number of INEEL-specific  $K_d$  measurements have been used to develop a set of default partition coefficients for use in screening investigations (DOE-ID 1994). In a review of the Interim Risk Assessment (Becker et al. 1998), the USGS (2000) concluded that these default parameters could not be shown to be conservative. The default parameters also cannot be shown to be representative because there is no site-specific basis for comparison. This issue is addressed in PSQ-1 through the measuring of the range of  $K_d$  values on sedimentary interbed samples collected in the vicinity of the SDA. Through either parametric or nonparametric methods, a  $K_d$  value can be selected from this range (representative) that is less than most of the values in the range (conservative). The data needed to address PSQ-1 are measured  $K_d$  values on samples collected from interbed material in the vicinity of the SDA. Additional factors to be considered include the following:

- Samples should come from both the 110-ft and 240-ft interbeds (also known as the B-C and C-D interbeds, respectively)
- Samples should come from wells distributed across the area
- A range of materials should be sampled that represents the range of anticipated adsorption characteristics
- Water chemistry of test solutions must be representative of vadose zone water at the SDA.

No quantitative statistical uncertainty can be established for determination of the range of  $K_d$  values for sedimentary interbeds at the SDA. Sampling locations will be qualitatively evaluated to determine whether the area around the SDA has been adequately represented and whether the range of materials encountered in the sedimentary interbeds has been adequately represented in the sampling.

#### 2.4.2 Principal Study Question 2

Adsorption can follow a linear isotherm, or it can follow a nonlinear isotherm where adsorption efficiency changes with concentration. If adsorption efficiency decreases with increased concentration, then retardation will decline as contaminant concentrations increase. Measurements of adsorption of strontium on INEEL interbed sediments collected at the Idaho Nuclear Technology and Engineering Center (INTEC) demonstrated nonlinear isotherms (Del Debbio and Thomas 1989; Liszewski et al. 1998). The computer code TETRAD can use either linear or Freundlich isotherms for predicting contaminant migration. The data needed to address PSQ-2 included measuring adsorption isotherms over a range of contaminant concentrations. Data to address PSQ-2 are being collected under contract to Clemson University,<sup>a</sup> and will not be included as part of this investigation.

#### 2.4.3 Principal Study Question 3

Contaminants adsorbed to a sediment may not desorb from the sediment when solution concentrations drop. Data needed to address PSQ-3 include measuring partition coefficients for desorption of contaminants from sediments. If the adsorption and desorption coefficients ( $K_d$  values) differ at the 95% confidence level, then it will be concluded that adsorption is not a reversible process. Computer simulation codes such as TETRAD cannot currently make use of this information. However, if contaminants do not readily desorb from sediments, it supports the conservatism of a simulation based on reversible adsorption.

#### 2.4.4 Principal Study Question 4

The chemistry of the solution is a significant factor in the amount of a contaminant available to partition to the solid phase. Ligands in solution form complexes with contaminants and hold the contaminant in solution. Cations in solution compete with contaminants for adsorption sites. Measurement of adsorption must assess the effect of chemistry, and to be defensible as a conservative measurement, must show that the worst chemical conditions relevant to the RWMC have been considered. Data to address PSQ-4 support using adsorption coefficients measured in waters of different chemical compositions representative of the vadose zone water at the SDA.

#### 2.4.5 Principal Study Question 5

Measured  $K_d$  values tend to show a large range of variation (Dicke 1997a), which has led to a general lack of faith in  $K_d$  values as a predictive tool. Whether the variation in  $K_d$  values can be accounted for by material properties of the sediments is answered by PSQ-5. If the variation in  $K_d$  can be explained by variations in material properties, then the mystery of  $K_d$  values is diminished and the utility of site-specific  $K_d$  values is enhanced.

Mechanistic models of adsorption attribute adsorption to electrostatic processes (ion exchange) on clay minerals and coulombic attractive forces (surface complexation) on the surface of oxide minerals (Turner and Sassman 1996). Data about the following sediment properties that will affect these processes are required to address PSQ-5, as well as the measured  $K_d$  values:

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a. Modification to Contract K99-181044, December 1, 1999, *Addition of Task 7 to Determine Partition Coefficients for Chromium, Uranium, Neptunium, and Americium in Composite Interbed Samples Collected from the Subsurface Disposal Area at the INEEL.*

- Surface area
- Mineralogy (bulk and clay)
- Cation exchange capacity
- Extractable iron, manganese, and aluminum oxides.

A stepwise multiple regression technique will be used to model the variation in measured  $K_d$  values on the measured soil properties. An  $F$ -test at the 90% confidence level on the change in residual sum of squares will be used to determine whether introduction of a soil parameter explains a significant amount of variation in the measured  $K_d$  values.

#### **2.4.6 Principal Study Question 6**

One of the primary areas of uncertainty identified by the USGS review (USGS 2000) of the SDA risk assessment (Becker et al 1998) was the existence of fast flow paths through the vadose zone. High-permeability pathways through basalt and interbeds permit rapid percolation of water during periods of high recharge. Because high-permeability pathways in interbeds consist of larger grain-size material, the surface area of this material would be low (Thompson, Schafer, and Smith 1996). It is hypothesized that the more permeable material also has a lower retardation capacity. This information is not particularly useful if transport simulations use average properties for materials. However, if some spatial distribution of properties is incorporated, correlations between hydraulic and adsorption characteristics will greatly enhance the computer simulation. The data needed to address PSQ-6 include measured  $K_d$  values and associated saturated hydraulic conductivities on comparable material. Intact core must be used for the hydraulic parameter measurements, and so samples cannot be split to use identical material for both hydraulic and geochemical characterization. The proximity of the core and visual comparability will be used to evaluate comparability.

A regression analysis will be performed between the measured  $K_d$  values and saturated hydraulic conductivity values measured on comparable materials. If the regression equation is significant at the 90% confidence level, then it will be concluded that there is a significant correlation between hydraulic properties and adsorptive properties and that incorporation of this relation in the risk analysis simulation will enhance the predictive model.

### **2.5 Test Approach**

The material to be used for this study is sedimentary interbed material from the vicinity of the SDA. No new wells will be drilled to collect samples. Samples will be derived from previously collected core. Seven wells immediately adjacent to the SDA that have core or sediment samples available from both the 110-ft and 240-ft interbeds will be selected. Both the 110-ft and 240-ft interbeds will be sampled with a second sample collected from either of the interbeds for a total of three samples per well. Two duplicates will be collected for a total of 23 samples. Samples will be paired (to the extent practicable) with samples submitted for hydraulic property characterization for the *Field Sampling Plan for the Radioactive Waste Management Complex Drilling and Core Sampling Project* (Casper 1999).

Kinetic experiments will be performed first to assess the conditions under which to run laboratory experiments. Adsorption parameters will be measured at concentrations that will not result in precipitation of secondary mineral phases. Test solutions will reflect the range of vadose zone water chemistry measured in lysimeters and perched zone monitoring wells at the SDA. Adsorption will be measured for americium, uranium, neptunium, and plutonium. Desorption from the soils will be

determined to measure reversibility of adsorption. Soil samples will be characterized for properties that affect adsorption—mineralogy by x-ray diffraction; extractable oxides of iron, manganese, and aluminum; cation exchange capacity and exchangeable cations; and surface area.

Adsorption experiments will be performed following the American Society for Testing and Materials (ASTM) Method D 4319–93, “Standard Test Method for Distribution Ratios by the Short Term Batch Method” (ASTM 1993).

## 2.6 Test Parameters

The transport and fate of contaminants in geologic material are dependent on chemical and physical processes that govern the distribution of contaminants between the solid and aqueous phases. Adsorption of dissolved species onto solid phases involves three components:

1. A contaminant component consisting of the strength of binding between the contaminant and a surface site
2. A solid phase component consisting of the mineralogy and number of adsorption sites
3. A solution component consisting of the concentration of cations competing for adsorption sites, anions that can form soluble aqueous complexes of the contaminant, pH, and the oxidation-reduction (redox) potential.

The distribution is often quantified at thermodynamic equilibrium by the  $K_d$ , an empirically determined parameter. Many transport models for contaminants use  $K_d$  values to predict the extent of migration relative to the mean groundwater velocity (Kincaid, Morrey, and Rogers 1984).

The  $K_d$  for a contaminant X is defined in Kipp, Stollenwerk, and Grove (1986) by

$$K_d = \frac{[X]_s}{[X]_{eq}} \quad (2)$$

where

$K_d$  = distribution coefficient (mL/g)

$[X]_s$  = contaminant sorbed per unit mass of material (mg/g or pCi/g)

$[X]_{eq}$  = concentration of X in solution after equilibration with the solid material (mg/mL or pCi/mL).

Samples also will be analyzed for a suite of parameters that will affect adsorption onto the solids. The solid-phase parameters to be characterized on the samples are the following:

- Bulk and clay mineralogy
- Surface area
- Extractable oxides (iron, manganese, aluminum)
- Cation exchange capacity and exchangeable cations



- Grain-size distribution.

Statistical analysis will be used to quantify the relation between the mineral parameters and the measured adsorption coefficient. For example, instead of a  $K_d$  in milliliters/gram, an adsorption coefficient defined in terms of surface area can be defined as

$$K_A = \frac{K_d}{S_A} \quad (3)$$

where

$K_A$  = surface area distribution coefficient (mL/m<sup>2</sup>)

$S_A$  = specific surface area (m<sup>2</sup>/g).

Bertetti, Pabalan, and Almendarz (1998) found that when the  $K_d$  was normalized to a specific surface area for a range of materials, the surface area distribution coefficient showed much less variation than the mass based  $K_d$ .

Another way of making a  $K_d$  value more representative of actual conditions is to redefine the mass-based  $K_d$  value to one where both the dissolved and solid concentrations are expressed relative to a unit volume of water (USGS 2000):

$$K_r = \frac{[X]_{sv}}{[X]_{eq}} \quad (4)$$

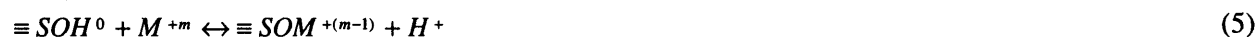
where

$[X]_{sv}$  = contaminant sorbed per unit volume of water (mg/mL or pCi/mL)

$K_r$  = volume / volume based distribution coefficient (dimensionless).

More sophisticated approaches are needed that allow the assumptions of constant geochemical conditions to be relaxed. Surface complexation models are based on the assumption that the formation of complexes with functional binding sites on mineral surfaces is analogous to the formation of aqueous complexes in bulk solution. The diffuse-layer model is one of the simplest of the surface complexation models that can still account qualitatively and quantitatively for the observed variation in experimental data (Dzombak and Morel 1990; Turner and Sassman 1996; Pabalan et al. 1998). The diffuse-layer model also is the model currently incorporated into the readily available geochemical computer simulation codes such as PHREEQC (Parkhurst and Appelo 1999) and Geochemist's Workbench (Bethke 1998).

Surface complexation is the formation of a chemical bond between an ion and a reactive surface site on a mineral surface. Cations in solution form complexes with the surface site as described by a chemical mass-balance reaction:



where the distribution of metal ion  $M^{+m}$  between the aqueous and solid phases at equilibrium is given by the equilibrium constant expression:

$$K_s = \frac{[\equiv SOM^{+(m-1)}][H^+]}{[\equiv SOH^0][M^{+m}]} \quad (6)$$

This reaction releases a hydrogen ion into solution, and so the equilibrium between the free metal in solution and the adsorbed metal on the surface will depend on the pH. At low pH, the metal may not be able to replace a hydrogen ion on the surface, and adsorption will be decreased.

The number of adsorption sites will be given by the surface area of the material, times the number of adsorption sites per unit area, and is equal to the sum of the free and complexed surface sites in Equation (6):

$$nS_A = \equiv SOH^0 + \equiv SOM^{+(m-1)} \quad (7)$$

The concentration of adsorbed metal  $[\equiv SOM^{+(m-1)}]$  is obtained by substituting Equation (7) into Equation (6) to replace  $\equiv SOH^0$ :

$$\equiv SOM^{+(m-1)} = \frac{K_s nS_A M^{+m}}{H + K_s M^{+m}} \quad (8)$$

In addition to forming complexes with surface sites, the metal can form aqueous complexes with ligands in solution. Formation of an aqueous complex also is a mass-balance reaction:



with an equilibrium constant expression given by

$$K_l = \frac{[ML^{+(m-n)}]}{[M^{+m}][L^{-n}]} \quad (10)$$

The total concentration of the metal  $M^{+m}$  in solution will be the sum of the free and complexed metal concentration

$$M_T = M^{+m} + ML^{+(m-n)} \quad (11)$$

Solving Equation (10) for  $ML^{+(m-n)}$  and substituting in Equation (11) gives an expression relating the total metal concentration and the free metal concentration:

$$M_T = M^{+m} + M^{+m} K_l L^{-n} = M^{+m} (1 + K_l L^{-n}) \quad (12)$$

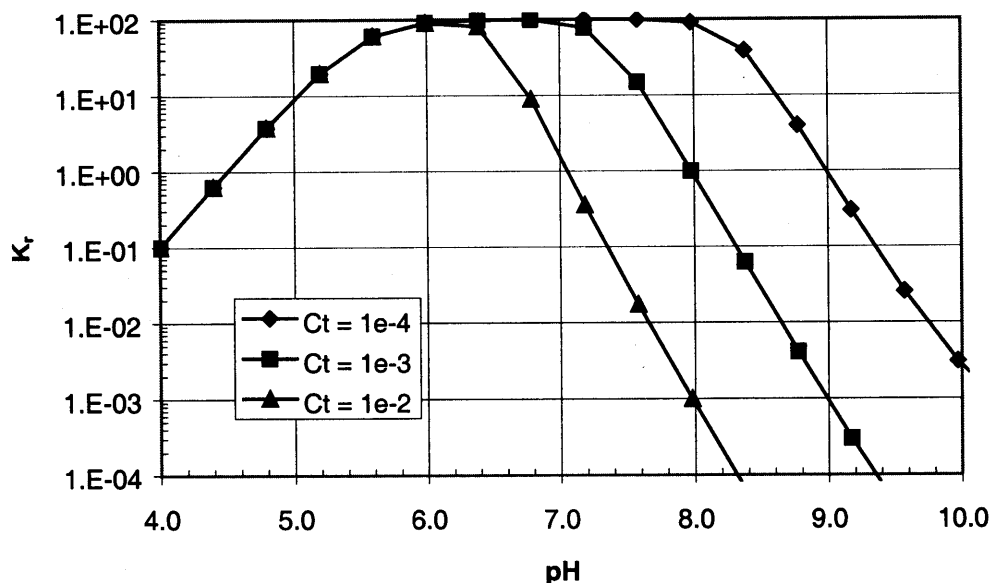
In terms of surface complexation theory, Equation (4) can be rewritten as

$$K_r = \frac{\equiv SOM^{+(m-1)}}{M_T} \quad (13)$$

Using Equation (8) for  $\equiv SOM^{+(m-1)}$  and Equation (12) for  $M_T$  in Equation (13) and simplifying gives an expression for adsorption that includes the effects of pH, surface area, and complexing ligands:

$$K_r = \frac{K_s n S_A}{[H + K_s M^{+m}][1 + K_l L^{-l}]} \quad (14)$$

This simple mechanistic approach can address pH effects, solution chemistry effects, and surface area effects on adsorption of metals onto minerals. This approach will permit addressing low or high pH values from waste solutions, complexing with organic chelating agents, and the formation of inorganic complexes with fluoride, phosphate, carbonate, or other ligands in solution. Figure 1 illustrates how the adsorption coefficient for a metal that forms an aqueous complex with a carbonate ion will vary as a function of pH and total dissolved carbonate concentration. The partition coefficient can vary over several orders of magnitude in the pH range of interest in the RWMC vadose zone (pH from 7.1 to 8.4).



**Figure 1.** Graph of the partition coefficient ( $K_r$ ) as a function of pH and total dissolved carbonate concentration ( $C_t$ ) in moles/liter.

### 3. EQUIPMENT AND MATERIALS

The equipment that is required for experiments testing sorption and desorption is standard laboratory equipment as mentioned below. A riffle splitter is required to ensure that the geologic material is divided without bias. Centrifuge tubes are required for each sorption experiment. An electronic balance is required to record the correct weight of the material in the centrifuge tubes to the nearest 0.1 mg. A shaker table or rotary mixer will be used to mix the solid and liquid at a constant rate and temperature. A centrifuge will be used to separate the supernatant from the supernate. The pH and conductivity of the solution before and after equilibration will be determined with a pH meter and a conductivity meter, respectively. A filtration system and an oven will be used to filter and dry the solids prior to determination of the desorption-sorption coefficients.

#### 3.1 Interbed Samples

Interbed samples were collected following procedures stated in the *Field Sampling Plan for the Radioactive Waste Management Complex Drilling and Core Sampling Project* (Casper 1999). Samples were collected from wells located outside of the SDA (Wells O-1 through O-9). Figure 2 is a map of the RWMC with the locations of wells drilled outside of the SDA for interbed sampling. Twenty-three samples will be collected from interbed material collected during this drilling campaign. The samples will be split: one portion will be sent to an analytical laboratory for characterization of material properties and the second portion will be used for adsorption experiments. Table 1 lists the samples to be collected from the core materials for this study.

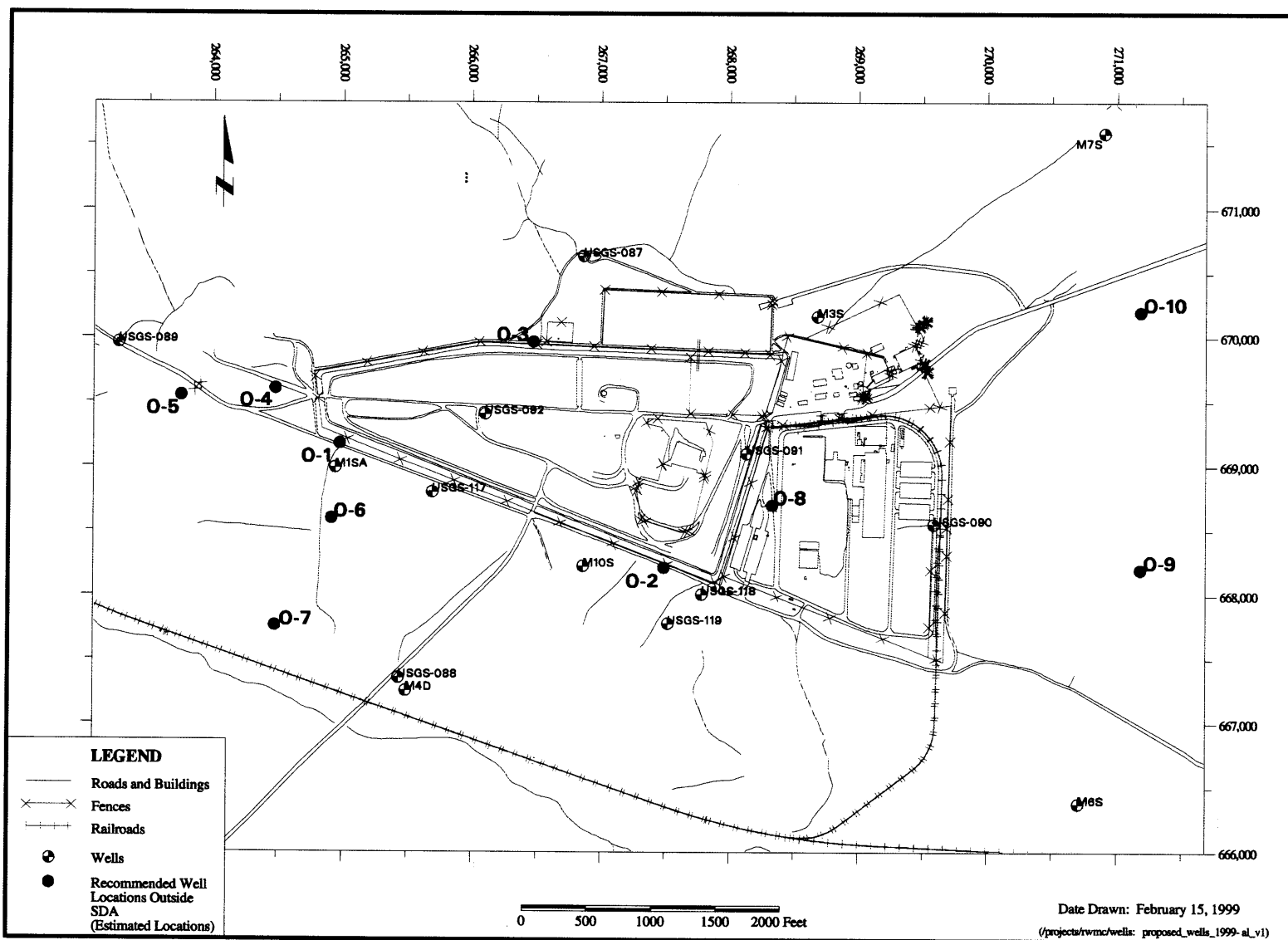
Interbed sample material from the SDA is highly variable in grain size. A visual assessment of sample material from the O-series wells indicates that some samples consist of silty clay, while other samples consist of gravel-sized rocks and cinders. Subsampling of gravel-sized material to obtain a representative sample is difficult. For example, a subsample of a gravelly material could consist of only one rock. Therefore, samples will be sieved to remove larger-sized particles prior to splitting for experiments. Adsorption is a surface area phenomenon (Bertetti, Pabalan, and Almendarz 1998). The contribution to surface area in a sample of sediment depends strongly on the particle size. Figure 3 illustrates how the contribution to surface area drops off as the particle size increases. Large particles (greater than about 1 mm) contribute little to the surface area of a sample. For purposes of this investigation, the sieve size used to remove the large-sized particles will be a 2-mm sieve, as recommended by the ASTM (1998), which corresponds to the upper size limit of sand-sized particles according to the Wentworth scale of particle size (Driscoll 1986).

Experiments will be conducted on the fine-grained material. If the mass of the larger particles is not accounted for in the final  $K_d$ , however, the adsorption will be overestimated. Therefore, if a sample is sieved to remove large particles, the final mass-based  $K_d$  will be adjusted by

$$K_d = K_{df} \frac{m_f}{m_t} \quad (15)$$

where

- $K_{df}$  = Partition coefficient measured on the fine size fraction (< 2-mm)
- $m_f$  = Mass of sample in the fine size fraction (< 2-mm)
- $m_t$  = Total sample mass.



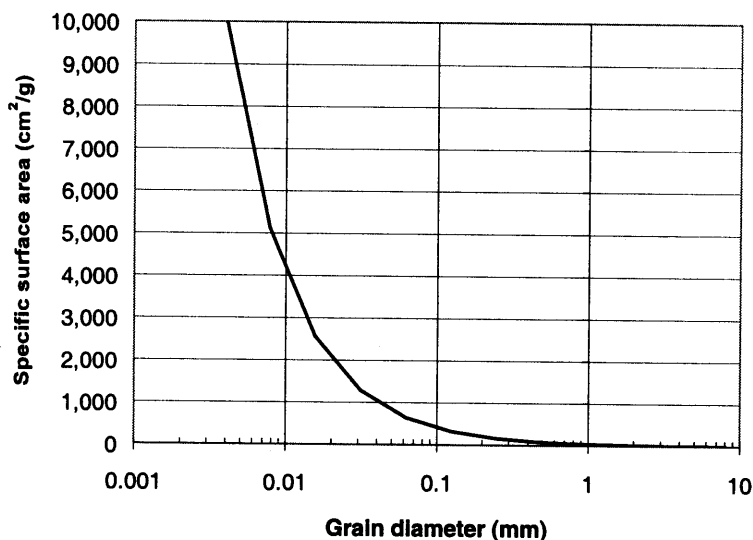
**Figure 2.** Map of the SDA with location of wells from which interbed samples were collected.

**Table 1.** Samples to be used to measure geochemical properties and adsorption coefficients.

Sample Number <sup>a</sup>	Sample ID	Location	Depth	Analysis <sup>b</sup>
3	7DS031013A	O-1	104.0-104.6	Suite 1
6	7DS033013A	O-1	110.0-110.7	Suite 1
11	7DS035013A	O-1	235.0-235.6	Suite 1
14	7DS037013A	O-2	110.9-111.4	Suite 1
17	7DS039013A	O-2	123.6-124.1	Suite 1
55	7DS08201A3	O-2	243-244	Suite 1
23	7DS043013A	O-3	97.5-98.0	Suite 1
26	7DS047023A	O-3	230.0-230.5	Suite 1
27	7DS047013A	O-3	234.1-234.7	Suite 1
57	7DS08401A3	O-5	111.5-113.5	Suite 1
58	7DS08501A3	O-5	117.8-118.8	Suite 1
59	7DS08601A3	O-5	126-127.3	Suite 1
60	7DS08701A3	O-5	126-127.3	Suite 1 (Duplicate)
56	7DS08301A3	O-5	249-250	Suite 1
61	7DS08801A3	O-6	108-109	Suite 1
62	7DS08901A3	O-6	118-119	Suite 1
63	7DS09001A3	O-6	243-245	Suite 1
64	7DS09101A3	O-7	134-135	Suite 1
65	7DS09201A3	O-7	148-149	Suite 1
66	7DS09301A3	O-7	148-149	Suite 1 (Duplicate)
67	7DS09401A3	O-7	245-248	Suite 1
68	7DS09501A3	O-9	136-137.4	Suite 1
69	7DS09601A3	O-9	144.7-145.7	Suite 1
70	7DS09701A3	O-9	229-230	Suite 1

a. Sample numbers for cross-referencing to Casper (1999) with additional samples (55 to 70) added for this test plan.

b. Analysis Suite 1 consists of grain-size distribution, surface area, bulk and clay mineralogy, cation exchange capacity and exchangeable cations, extractable oxides, and adsorption coefficients.



**Figure 3.** Distribution of surface area with grain size for spherical particles.

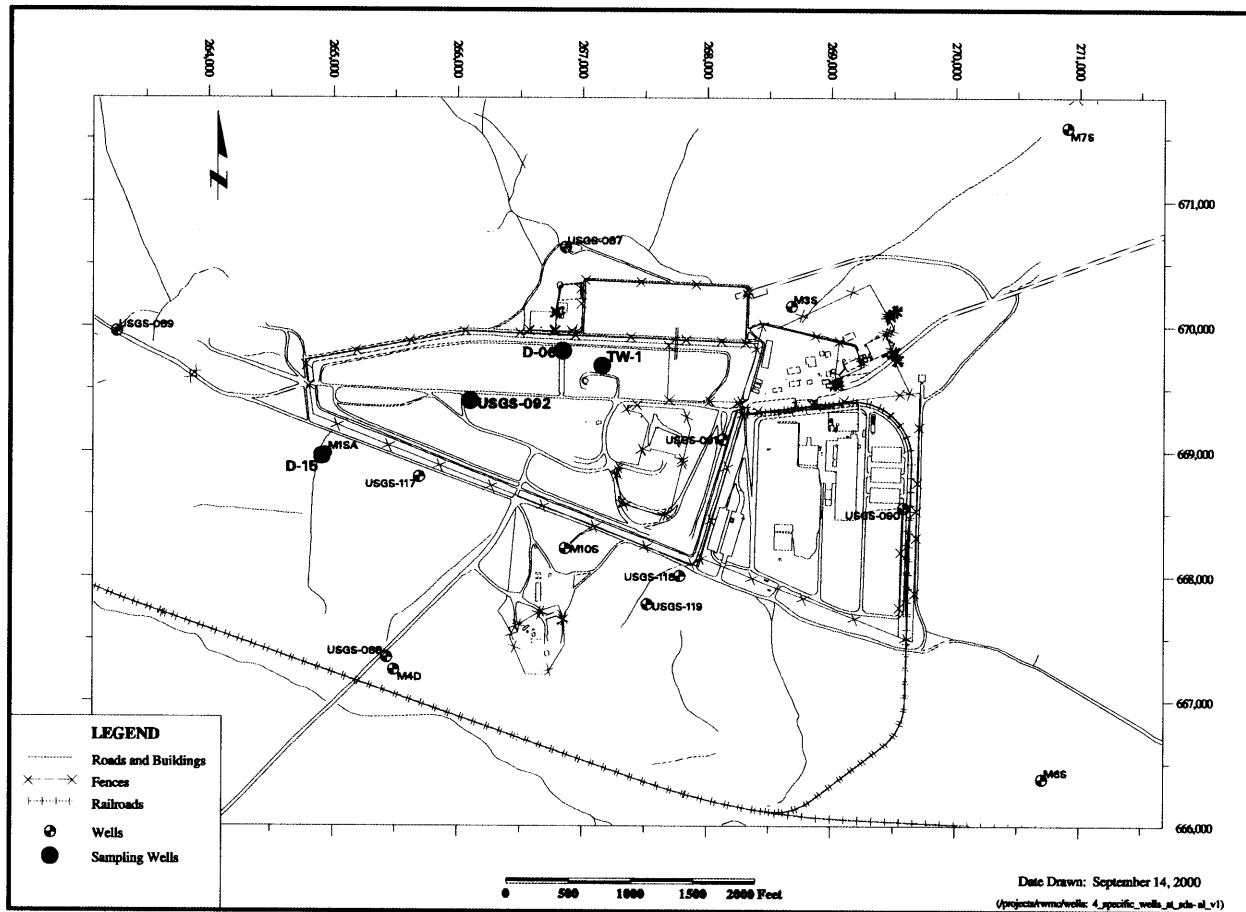
This correction approach incorporates the assumption that the gravel-sized material does not contribute to the adsorption capacity of a sediment. This approach may slightly underestimate the total sorption capacity of a sample, but is expected to have only a minor effect based on surface area considerations discussed above.

## 3.2 Test Solutions

In a review of the adsorption coefficients used in previous risk assessment calculations for the SDA, the USGS concluded that the  $K_d$  values could not be shown to be conservative because the test solutions used in the experiments did not adequately reflect the vadose zone water chemistry of the SDA (USGS 2000). Therefore, an important consideration for these experiments is the chemistry of the carrier solution for the tracers. The water must mimic the important characteristics of the vadose zone pore water so that the measured isotherms are representative of the SDA vadose zone. The chemistry of water samples from a perched water well (USGS-92) at the SDA, and water from suction lysimeters installed in the sedimentary interbeds at the SDA, were reviewed to develop the test solutions. Well locations are shown in Figure 4 and the water analyses are shown in Table 2.

### 3.2.1 Soil Water Composition

During the mid to late 1980s, a network of suction lysimeters was installed in the SDA to monitor soil-water chemistry (Laney and Minkin 1988). Water samples collected from these lysimeters can be used to define the expected soil water chemistry for pore water in the SDA. Similar analyses have been conducted before by Dicke (1997a, 1997b) and Hull and Pace (2000), but for different objectives. This analysis focuses on water samples from the deep vadose zone and does not include samples from surface sediments.



**Figure 4.** Map of the SDA with location of wells from which vadose zone perched water chemistry information is available.

A tracer test conducted by the USGS in 1999 showed that tracer added to the spreading areas west of the RWMC migrated laterally to Well USGS-92.<sup>b</sup> Therefore, water on the west end of the SDA (at Well USGS-92 and Lysimeter DL06) and in deeper interbeds at the east end of the SDA (at Well DL03) probably reflects recharge from the spreading areas.

Water on the east and north of the SDA is much higher in salt content than water at the west end of the SDA. This higher salt content is the result of a brine solution applied to roadways in the SDA to suppress dust. Waste disposal operations at the SDA generated large quantities of airborne dust from heavy equipment moving along dirt roads. Magnesium chloride brine was applied to selected RWMC roadways in 1984, 1985, 1992, and 1993 to control airborne dust. The brine migrated very rapidly in the

b. Presentation to the INEEL Groundwater Committee by Brennen Orr of the U.S. Geological Survey, September 28, 1999.



**Table 2.** Chemical composition of water in the vadose zone at the SDA as measured in suction lysimeters and perched water monitoring wells.

Well	Lysimeter	Depth (ft)	Date	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	HCO <sub>3</sub> (mg/L)	Chlorine (mg/L)	Iron (mg/L)	SO <sub>4</sub> (mg/L)	Bromine (mg/L)	NO <sub>3</sub> (mg/L)	Field pH	Temp (°C)
D06	DL01	88.0	9/9/98	691	426	1020	43.5	264.0	3420.0		1860.0	8.40	110.00	7.31	20.3
D06	DL02	44.0	6/17/88	707	678	2675	55.9	177.0	5270.0	0.39	2370.0	11.50		7.12	18.4
D06	DL02	44.0	8/2/88	708	688	2757	57.0	183.0	5420.0	<0.05	2390.0	11.40		7.78	14.8
D06	DL02	44.0	9/29/88	680	679	2774	60.0	193.0	5567.0	0.41	2375.0	7.30		7.15	12.4
D06	DL02	44.0	7/27/89	724	735	2937	61.5	229.0	5730.0	0.40	2612.0	10.50		7.27	20.3
D06	DL02	44.0	8/31/89	755	757	3035	62.1	221.0	5860.0	0.38	2575.0	11.30		7.12	14.0
D06	DL02	44.0	9/9/98	752	822	3180	86.5	449.0	7140.0		4380.0	12.80	94.00	7.55	18.5
TW1	DL04	101.7	6/16/88	804	417	595	29.7	182.0	2700.0	0.53				6.98	18.2
TW1	DL04	101.7	8/2/88	911	494	682	32.0	180.0	2990.0	<0.05	1090.0	33.00			
TW1	DL04	101.7	9/9/98					200.0	3280.0		489.0	6.10	61.00	6.98	15.8
TW1	DL03	226.9	6/16/88	33	8	222	3.1								
D15	DL06	97.9	6/16/88	53	18	254	3.8	284.0	135.0	0.90	314.0	3.60		8.10	19.8
D15	DL06	97.9	8/2/88	38	7	258	4.6	275.0	89.0	0.95	287.0	2.50			
D15	DL06	97.9	9/27/88	35	6	256	4.1	278.0	152.0	0.90	233.0				
USGS <sup>a</sup> 092		213.0	10/29/76	29	17	120	12.0	290	81	0.4	64	0.3		8.39	13.5
High TDS <sup>b</sup>		Median		724	679	2757	57	197	5345	0.4	2375	11.3	94	7.15	18
Low TDS		Median		35	8	254	4	281	112	0.9	260	2.5		8.25	17
		EPM <sup>c</sup> Cations		EPM Anions	Error										
High TDS		213.4		205.0	2.0 %										
Low TDS		13.5		13.2	1.1 %										

a. USGS = U.S. Geological Survey.

b. TDS = Total dissolved solids.

c. EPM = Equivalents per million.

soil water and was detected in some of the suction lysimeters by 1988. Ten years later in September 1998, samples collected from Lysimeters DL01, DL02, and DL04 showed that levels of sodium and chloride remained very high in these lysimeters, even though brine has not been applied at the SDA since 1993.

The data presented in Table 2 are not particularly comparable across time and space because routine SDA-wide monitoring of the instruments has not been conducted. From this available data, it appears that there are at least two very different water types under the SDA. A comment from the USGS (2000) in their review of the Interim Risk Assessment (Becker et al. 1998) stated that use of the adsorption isotherm approach will require demonstration that the geochemical conditions in the vadose zone were reasonably stable. The large difference in water chemistry measured in the deep lysimeters indicates that geochemical conditions are far from stable in the vadose zone under the SDA. Because there are two different geochemical regimes in the vadose zone under the SDA, a single, representative water sample cannot be identified. Therefore, two representative waters were defined.

At the bottom of Table 2, median concentrations are shown for the western, low total dissolved solids water and the eastern, high total dissolved solids water. The two median compositions are defined as the two representative water compositions for the vadose zone at the SDA. Two methods can be used to develop representative water samples. One method is to collect water from a lysimeter or well closest in chemistry to the median water chemistry. There is no easy way to collect a large quantity of water from the subsurface at the SDA to conduct the laboratory tests. Therefore, the second alternative, preparing synthetic solutions in the laboratory to mimic the natural water samples, will be used. Recipes for synthesizing the two representative water types in the laboratory are shown in Table 3 for the eastern, high total dissolved solids water, and in Table 4 for the western, low total dissolved solids water. These solutions will be used as carrier solutions for the radioactive tracers used in the adsorption experiments. Sodium hydroxide or hydrochloric acid will be used to adjust the final pH of the synthetic solution to give the median pH value listed in Table 2.

### 3.2.2 Tracers

Tests must measure adsorption of tracers and not other processes, such as precipitation of solid phases. Therefore, the concentrations of tracers must be low enough to prevent precipitation of solid phases. Geochemical calculations were performed to evaluate the maximum concentration of tracers that can be used in solution without resulting in precipitation of minerals. The solubility calculations were performed using the PHREEQC computer code (Parkhurst and Appelo 1999) and the COM\_R6\_V8 thermodynamic database from Lawrence Livermore National Laboratory.

Two synthetic soil water solutions will be prepared following the recipes defined above. The synthetic vadose zone waters will then be spiked with radioactive tracers. A solution tracer concentration of one-half of the solubility limit was identified as the maximum allowable concentration to prevent precipitation of solid minerals. The minerals found to limit the solubility and the maximum allowable concentrations for each synthetic water are shown in Table 5.

The amount of tracer remaining in solution after equilibration must be measurable. The lowest tracer concentration remaining was selected at two times the detection limit. The amount of tracer adsorbed during an experiment is given by

$$[X]_s = ([X]_i - [X]_{eq}) \frac{V}{m} \quad (16)$$

where

**Table 3.** Recipe for eastern, high total dissolved solids synthetic vadose zone water.

Compound	Formula Weight (g/mole)	Amount Needed (mg/L)	Amount Needed (moles/L)
NaCl	58.44	1919.75	3.28E-02
NaOH	40.00	1966.34	4.92E-02
NaHCO <sub>3</sub>	84.01	207.22	2.47E-03
Na <sub>2</sub> CO <sub>3</sub>	105.99	65.49	6.18E-04
NaF	41.99	1.04	2.48E-05
Na <sub>2</sub> SO <sub>4</sub>	142.04	1791.96	1.26E-02
Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	212.14	40.60	1.91E-04
MgCl <sub>2</sub> ·6H <sub>2</sub> O	203.31	5678.88	2.79E-02
CaCl <sub>2</sub> ·2H <sub>2</sub> O	147.02	2655.51	1.81E-02
H <sub>2</sub> SO <sub>4</sub>	98.08	1150.82	1.17E-02
HCl	36.46	1006.30	2.76E-02
K <sub>2</sub> SO <sub>4</sub>	174.27	65.35	3.75E-04
KOH	56.11	23.47	4.18E-04
K <sub>2</sub> CO <sub>3</sub>	138.21	19.95	1.44E-04

**Table 4.** Recipe for western, low total dissolved solids synthetic vadose zone water.

Compound	Formula Weight (g/mole)	Amount Needed (mg/L)	Amount Needed (mole/L)
NaOH	40.00	113.40	2.84E-03
NaHCO <sub>3</sub>	84.01	205.41	2.45E-03
Na <sub>2</sub> CO <sub>3</sub>	105.99	205.17	1.94E-03
Na <sub>2</sub> SO <sub>4</sub>	142.04	107.50	7.57E-04
Na <sub>2</sub> SiO <sub>3</sub> ·5H <sub>2</sub> O	212.14	40.60	1.91E-04
MgCl <sub>2</sub> ·6H <sub>2</sub> O	203.31	21.25	1.05E-04
MgCO <sub>3</sub>	84.32	18.91	2.24E-04
CaCl <sub>2</sub> ·2H <sub>2</sub> O	147.02	124.86	8.49E-04
CaF <sub>2</sub>	78.08	1.86	2.38E-05
H <sub>2</sub> SO <sub>4</sub>	98.08	189.47	1.93E-03
HCl	36.46	56.15	1.54E-03
K <sub>2</sub> SO <sub>4</sub>	174.27	3.15	1.81E-05
KOH	56.11	3.71	6.61E-05

**Table 5.** Maximum tracer concentrations to be used in experiments to avoid precipitation of solid phases.

Element Mineral Control	High TDS <sup>a</sup> Water, Solubility Limit (moles/L)	Low TDS Water, Solubility Limit (moles/L)	One-Half the Lesser Solubility (moles/L)	Maximum Activity in Solution and Isotope (pCi/L)
Americium AmOHCO <sub>3</sub>	6.7E-07	6.0E-08	3.0E-08	2.5E+07 (Am-241)
Neptunium NpO <sub>2</sub>	5.3E-06	8.4E-07	4.2E-07	7.0E+04 (Np-237)
Plutonium PuO <sub>2</sub>	1.2E-12	2.0E-12	6.1E-13	2.5E+03 (Pu-238)
Uranium Soddyite	1.0E-06	3.6E-06	5.0E-07	2.6E+02 (U-235)

a. TDS = total dissolved solids.

$[X]_i$  = initial concentration of tracer in solution (pCi/mL)

V = volume of solution (mL)

m = mass of solid phase (g).

The final solution concentration should remain above the detection limit ( $D_l$ ) to ensure that a partition coefficient can be defined. At a minimum then

$$\begin{aligned} [X]_{eq} &\geq 2D_l \\ [X]_s &\geq K_d 2D_l \end{aligned} \quad (17)$$

Substituting back into Equation (16), and using a solution volume of 30 mL and a soil mass of 5 g, the minimum  $[X]_i$  that will result in a measurable  $X_{eq}$  can be calculated:

$$2D_l \left( \frac{m}{v} K_d + 1 \right) = [X]_i \quad (18)$$

The calculated  $[X]_i$  values are shown in Table 6. Tracer concentrations used for the experiments need to be between the minimum concentration calculated in Table 6 and one-half the solubility limit listed in Table 5. For plutonium, a number of adsorption coefficients have been used for INEEL risk assessment

projects. If the plutonium adsorption coefficient is near the low range used, then there will be no difficulty detecting Pu-238 in experiments. If adsorption is the high end of the range, then the calculated minimum starting concentration is larger than the solubility limit. Because precipitation from a supersaturated solution would invalidate adsorption experiments, the solubility limit is considered the more important limiting parameter. If meaningful  $K_d$  measurements cannot be obtained for plutonium using these experimental conditions, an alternative design will be developed following a similar procedure, but changing the water-to-solid ratio. Table 7 lists the approximate concentrations of the tracers in the test solutions to be used in the sorption experiments.

**Table 6.** Calculation of minimum starting concentration to ensure measurable adsorption during experiments.

Species	$K_d^a$ (mL/g)	Detection Limit (pCi/L)	Volume (mL)	Mass (g)	Minute $[X]_i$ (pCi/L)
Am-241	450	0.5	30	5	2,700
Np-237	8	0.5	30	5	50
Pu-238	5100	0.5	30	5	30,600
Pu-238	20 <sup>b</sup>	0.5	30	5	120
U-235	6	0.5	30	5	40

a. Magnuson and Sondrup (1998, Table 2).

b. Waste Area Group 3, OU 3-13, Comprehensive Remedial Investigation/Feasibility Study (Rodriguez et al. 1997; DOE-ID 1997).

**Table 7.** Tracer concentrations in picocuries/liter for test solutions.

Species	Tracer Concentration (pCi/L)
Am-241	5,000
Np-237	5,000
Pu-238	2,500
U-235	200

### 3.2.3 Valence State of Tracers

Actinides can occur in several different valence states, and the valence state can significantly affect adsorption. Adsorption experiments should be conducted under redox conditions representative of the vadose zone at the SDA so that the valence state of the actinide is representative. Dissolved oxygen measurements of water samples collected from lysimeters at the SDA and the high air permeability of the vadose zone indicate that oxidizing conditions are expected. Under oxidizing conditions, the anticipated valence states for the actinides in solution are uranium in the +6 valence state, neptunium in the +5 valence state, americium in the +3 valence state, and plutonium the +5 valence state.

The speciation of plutonium, in particular, is quite sensitive to pH, redox conditions, and concentrations of complexing ligands such as carbonate and fluoride. Laboratory column experiments were conducted at Clemson University<sup>c</sup> where plutonium+4 and plutonium+5, as tracers in synthetic groundwater, were flushed through columns packed with interbed material from the SDA.

c. Presentation of unpublished data at a subcontract technical review, Robert A. Fjeld, John T. Coates, and Alan W. Elzerman, Clemson University, August 2000.

Plutonium in the +4 valence state was strongly sorbed to column sediments in the absence of complexing agents. Plutonium+5 was likewise strongly sorbed to column sediments, and the conclusion of the study was that the plutonium+5 reacted with the sediments and was reduced to plutonium+4. The valence state in the vadose zone and in the laboratory batch experiments will likely be controlled by reactions between dissolved plutonium and minerals in the sediments. The experiments will be conducted with plutonium+5 as the starting material.

## 4. EXPERIMENTAL PROCEDURES

The procedures that will be followed to carry out the experiments are discussed in this section.

### 4.1 Material Characterization

Mineralogy will be determined by x-ray diffraction following methods described in Klute (1986, Chapter 12). Mineral identification is made by matching peaks in x-ray diffraction patterns to peaks recorded in libraries of known minerals such as the compilations of Brown and Brindley (1980) or the Hanawalt or Fink indexes in the *Mineral Powder Diffraction File* (JCPDS 1980).

Adsorption is a surface phenomenon. Surface area of the material will be determined by multipoint nitrogen absorption using Brunauer-Emmett-Teller surface area analysis (Brunauer, Emmett, and Teller 1938).

Sorption generally occurs on the oxide coatings of sediments. To develop a surface complexation model for sorption of various metals to each other, determining the amount of oxides present on the soil following the method described by Klute (1986, Chapter 5, Section 5-4) is necessary. The determination is made by placing approximately 4 g of material in a centrifuge tube and adding 40 mL of sodium citrate followed by 5 mL of sodium bicarbonate. The centrifuge tube is then placed in a water bath and warmed to 80°C. Solid sodium dithionite is added to the mixture and stirred. Sodium chloride is then added to induce flocculation. If flocculation does not occur, acetone is added. The suspension is then mixed and warmed in a water bath to expedite flocculation. Finally, the suspension is centrifuged and the supernatant decanted. The concentrations of iron, manganese, and aluminum are determined in the supernatant by inductively coupled plasma emission spectrometry (ICP) (U.S. Environmental Protection Agency [EPA] Method 200.7 or 200.8) or atomic absorption (AA) (EPA Method 236, 243, and 202 respectively for iron, manganese, and aluminum) (Mueller and Smith 1992).

The cation exchange capacity (CEC) of the soil or clay is an important characteristic that aids in evaluating the sorption process. The CEC is determined following Page, Miller, and Keeney (1982, Chapter 8). To determine the CEC of soil, all of the exchange sites are first saturated with sodium. Saturation is accomplished by placing approximately 5 g of material in a centrifuge tube and 30 mL of 1.0 M sodium acetate. A pH adjusted to 8.2 is added. The centrifuge tube is shaken for 5 minutes and then centrifuged until the supernatant is clear. The supernatant is decanted and discarded. This process is repeated four more times. All of the exchange sites are now saturated with sodium. This same process is repeated three more times using 95% ethanol instead of sodium acetate to remove water. The sodium filling all of the exchange sites is extracted by repeated equilibrations and separations with 1.0-M ammonium acetate, with the pH adjusted to 7.0. The supernatant is collected after the each repetition, diluted to 100 mL, and analyzed for sodium by AA or ICP (EPA 200 series methods) (Mueller and Smith 1992). The CEC is calculated using

$$CEC(meq/100g) = \frac{100 \cdot Na(mg/l) \cdot 0.1(l)}{23.0(mg/meq) \cdot m(g)} \quad (19)$$

where

Na = sodium concentration in extract (mg/L)

m = mass of sample extracted (g).

The cations present in the soil participate in sorption via ion exchange processes. Different cations compete for ion exchange sites differently. Therefore, the cations present on the soil need to be determined so that a better understanding of the sorption process on soils can be developed. Cations present on soil are determined following the process of Page, Miller, and Keeney (1982, Chapter 9). This process is similar to the method of determining total CEC. However, the first step of saturating the exchange sites with sodium is bypassed. Ammonium acetate is used to extract the ions naturally occupying the exchange sites. The ammonia will replace all of the cations on the soil leaving a solution with all of the exchangeable cations. The collected solution is analyzed for calcium, sodium, magnesium, aluminum, strontium, potassium, and iron by the ICP or AA (EPA 200 series methods).

## **4.2 Adsorption Experiments**

Adsorption experiments will be performed following the ASTM method D 4319-93, "Standard Test Method for Distribution Ratios by the Short Term Batch Method" (ASTM 1993). All solid materials will be dried at 60°C prior to weighing for test procedures.

### **4.2.1 Soil Pre-equilibration**

Solids and test solutions are not likely to be in equilibrium, which may lead to unwanted geochemical reactions during adsorption experiments. Solids and test solutions are pre-equilibrated before beginning the adsorption experiments. The solid sample will be washed three times for 15 minutes each with the test solution without the radioactive tracer. After the 15-minute equilibration time, the mixture will be centrifuged at 1,400 g or more for 20 minutes, and the supernatant decanted. The pH and specific conductance of the supernatant will be measured and recorded. The sample will be washed a fourth time for 24 hours, mixing occasionally. The fourth wash solution will be spiked with tracer in the centrifuge tube to conduct the test. The mass of solid is measured prior to washing by weighing the centrifuge tube. The volume of solution added for the adsorption experiment is obtained by weighing the centrifuge tube after the spike solution has been returned to the tube.

### **4.2.2 Kinetic Experiments**

Prior to batch experiments, a kinetic experiment will be run to determine the time for sorption to reach equilibrium. Kinetic experiments will be run in each vadose zone water on one randomly selected interbed material. Approximately 1 g of geologic media, prewashed with test solution, is mixed with 30 mL of synthesized solution with the tracer isotopes added. The tubes are placed on the shaker table or rotary mixer. One tube is removed at a time at various time intervals, centrifuged at a minimum of 1,400 g for 20 minutes, decanted, filtered through a 0.1- $\mu$  filter, acidified, and sent for analysis. Two blanks for each vadose zone water spiked with tracers will be prepared. The first blank will never be placed on the shaker table or rotary mixer but will be analyzed immediately. The second blank will be collected and analyzed with the final reaction tube. Fourteen tubes are needed for each experiment: two blanks, one tube each to be sampled at the approximate times of 0.1 hour, 1 hour, 3 hours, 7 hours, 24 hours, 32 hours, 48 hours, 56 hours, 72 hour, and 96 hours. The pH and conductivity will be measured in the solution remaining in the tube after centrifugation and removal of the aliquot for tracer analysis. The data obtained from the kinetic experiments are used to determine the equilibration time for adsorption. Once the equilibration time is determined, then each batch experiment is run for that amount of time.

### **4.2.3 Sediment Radionuclide Concentrations**

The experimental approach used in these experiments is based on the assumption that there are no significant levels of the radioactive tracers present in the soil prior to the experiment. Four samples will be analyzed for total extractable Am-241, Np-237, Pu-238, and U-235. No americium, neptunium, or



plutonium are expected in these samples. Uranium-235 occurs naturally at concentrations about 2 pCi/g. Because 500 pCi will be added to each reaction tube at the beginning of the experiment, the naturally occurring levels of U-235 will not be significant.

#### **4.2.4 Batch Experiments**

Adsorption experiments will be conducted in each of two representative SDA vadose zone waters. Adsorption studies will be performed in 50-mL polyethylene centrifuge tubes. The geologic media will be homogenized and riffle-split (to avoid bias) to the appropriate amount (~1 g), and then placed in the centrifuge tubes. The geologic media will be pre-equilibrated to the test solutions (without tracer) by washing the soil with 30 mL of the test solution three times prior to the experiment. A fourth washing of test solution will then be allowed to equilibrate with the soil for 24 hours. Solution used for the fourth washing/equilibration will be left in the tube, and the pH and specific conductance will be measured and recorded in an environmental restoration logbook. A small volume (0.1 to 0.5 mL) of solution containing radioactive tracers will then be spiked into the centrifuge tube to give the desired initial tracer concentrations. Each experiment consists of triplicate samples of 1 g of geologic media mixed with 30 mL of synthesized solution spiked with radioactive tracers in each of two representative vadose zone waters, blanks consisting of centrifuge tubes without geologic material spiked with the tracers in each of the vadose zone waters, and blanks of carrier solution and soil without tracer. All of the centrifuge tubes will be placed on a shaker table or rotating mixer for the appropriate duration. Once the experiment is complete, the centrifuge tubes are taken off the shaker table and centrifuged at a minimum of 1,400 g for 20 minutes. The supernatant is decanted, filtered through a 0.1- $\mu$  filter, acidified, and sent for isotopic analysis. A final pH and conductivity measurement will be made in the solution remaining in the centrifuge tube (~10 mL).

The supernatant from the carrier blanks (vadose zone water plus sediments without tracer) will be analyzed for bulk water chemistry. Total alkalinity will be determined by titration with standardized acid. Anions (i.e., chloride, sulfate, nitrate, and phosphate) will be determined by anion chromatography, and cations (i.e., calcium, magnesium, sodium, potassium, strontium, and aluminum) will be determined by ICP.

### **4.3 Desorption Experiments**

Desorption and leaching experiments will be performed on the geologic material after sorption experiments. The experiments will be used to test the reversibility of sorption by developing desorption partition coefficients. Desorption coefficients will then be compared to the adsorption coefficients to test the reversibility of the sorption process. The solid material from the sorption isotherm experiments will be the stationary phase, and the mobile phase will be the synthetic soil water solutions without a spike of the radioactive tracer. The tracer solution from the adsorption experiments will be decanted from the centrifuge tubes, leaving as small a volume of residual water as practicable. The solid material and residual water will be weighed to calculate the amount of carryover from the adsorption experiments. The synthesized vadose zone water will be added to each tube. The tubes will then be placed on the rotary mixer for the same duration as the batch experiment. After equilibration, the tubes will be taken off the mixer and centrifuged, and the supernatant will be decanted, filtered through a 0.1- $\mu$  filter, and acidified. The pH and conductivity of the solution remaining in the tubes will be measured and recorded. The supernatant will then be analyzed for tracers by liquid scintillation analyses.

## 4.4 Isotopic Analysis

Isotopic analysis of U-235, Np-237, Pu-238, and Am-241 in solution after equilibrium must be performed to determine the sorption isotherm distribution coefficients. The analysis for all isotopes will be performed by scintillation counting following manufacturer procedures as incorporated in *Analytical Chemistry Method Manual 3200* and *Analytical Chemistry Method Manual 3993* for the radioanalytical laboratory at the INTEC. Approximately 5 mL of the equilibrium solution per centrifuge tube are needed for isotopic analysis. Liquid scintillation counting has a lower detection limit for short-lived isotopes than conventional methods of elemental analysis such as ICP. The concentrations will be reported as picocuries/liter or curies/liter.

## 4.5 Data Analysis

Adsorption and desorption partition coefficients will be developed to determine the distribution coefficient for a given range of solution concentrations. The sorption parameters will then be used in transport modeling of contaminants. All  $K_d$ s will be corrected to the original mass of the sample prior to sieving by assuming that there is no adsorption on particles smaller than 2 mm. Values for  $K_d$  will be provided to the modeler upon completion of the  $K_d$  study.

## **5. WASTE MANAGEMENT**

Waste generated during this project includes less than 1 kg of soil contaminated with small amounts of short-lived isotopes, aqueous solutions with small amounts of short-lived isotopes solidified on corncobs, disposable protective clothing and supplies, centrifuge tubes, scintillation vials, and disposable pipets contaminated with short-lived isotopes. All waste generated will be combustible low-level radioactive waste. No hazardous or mixed waste will be generated during this project. All waste will be managed and disposed of in coordination with the INTEC representative for Waste Generator Services.

## **6. KEY PROJECT PERSONNEL**

This project will involve the following key types of personnel: project manager, scientists, analytical chemists, and laboratory technicians. The role of the project manager will be to oversee the project and to ensure that it is performed on schedule and within the budget. The scientists involved in this project will prepare the test plan, perform the experiments and make any technical decisions necessary during the project, analyze and interpret data, and write the final report. The laboratory technicians will perform laboratory work in accordance to the test plan under the directions of the scientists. The analytical chemists will analyze the samples using standard radioanalytical laboratory analytical procedures after experimentation and ensure that the data are interpreted correctly. In addition, a publication editor will edit all publications prepared as a result of this project.

## 7. QUALITY ASSURANCE/QUALITY CONTROL

Quality control of the data obtained from the sorption and desorption experiments will be measured by running replicate reaction tubes. Each adsorption or desorption coefficient will be run in triplicate and the uncertainty calculated from the statistics on the triplicate measurements. Two soil samples will be submitted as duplicates to further measure the uncertainty in the measurement technique.

Blanks, consisting of a centrifuge tube filled with solution spiked with tracers but no soil, will be used to measure the potential for centrifuge tubes to adsorb the contaminant.

The quality assurance program will follow the *Quality Assurance Project Plan for the Analytical Laboratories Department Radioanalytical Section* (INEEL 1997) and the "Quality Assurance Project Plan for Waste Area Groups 1, 2, 3, 4, 5, 6, 7, 10, and Inactive Sites (Draft)" (DOE-ID 2000).

## **8. HEALTH AND SAFETY**

Health and safety issues will be addressed through Management Control Procedure (MCP) -3571, "Independent Hazard Review," and MCP-005, "Chemical Hygiene Plan," which are maintained by Applied Engineering and Development Laboratory.

## **9. DELIVERABLES**

Site-specific adsorption parameters for the actinides uranium, neptunium, plutonium, and americium will be determined for sedimentary interbed materials at the SDA. Weekly and monthly progress reports will be submitted to the project manager. A final report will be written.

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